Chirality in Complexes

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Aza[6]helicene Platinum Complexes: Chirality Control of *cis–trans* Isomerism**

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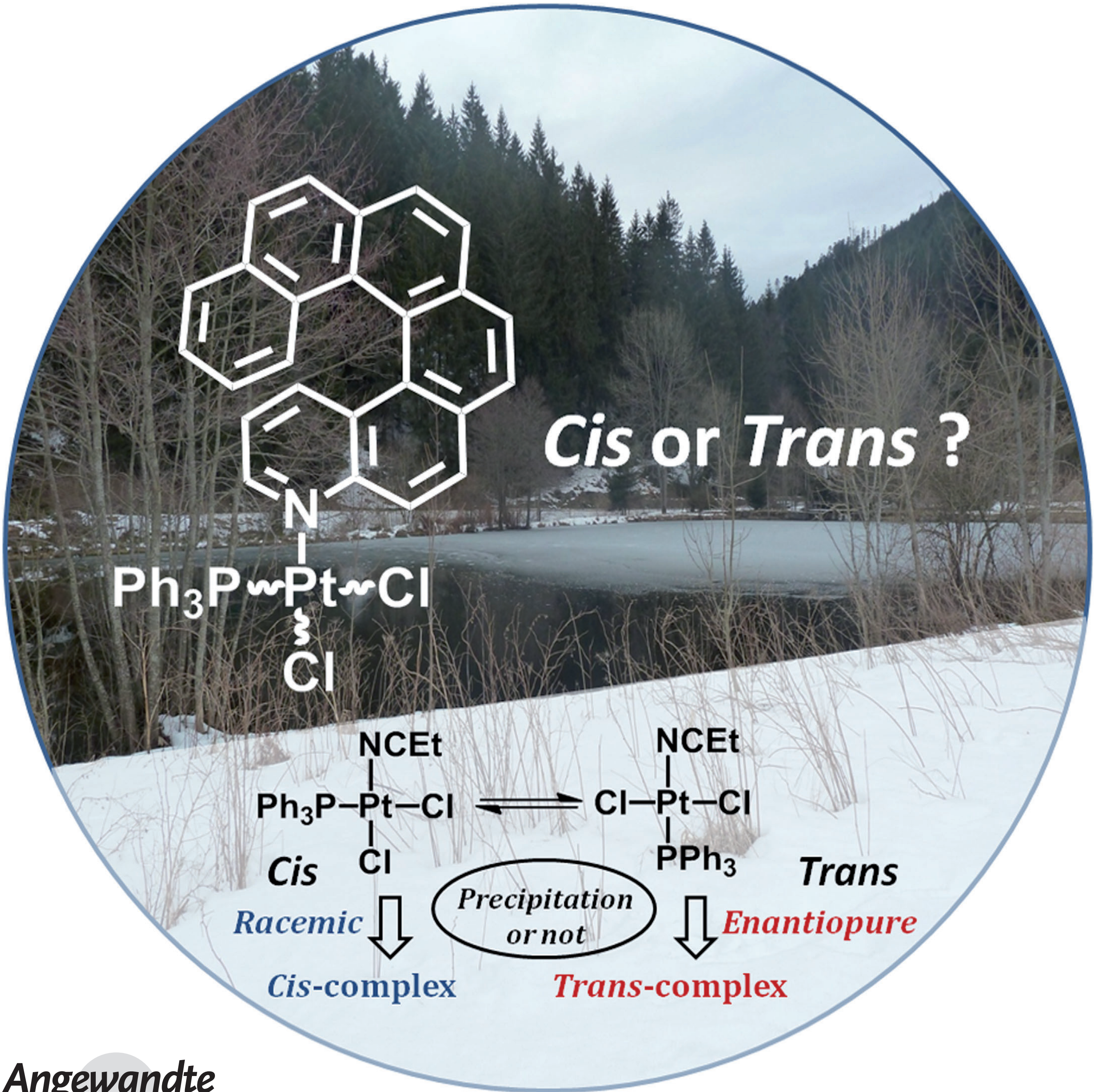


Abstract: *It was serendipitously observed that cis-[$PtCl_2$-(NCEt)PPh_3] reacted differently with either racemic or enantiopure 4-aza[6]helicene, giving respectively cis (racemic) and trans (enantiopure) [$Pt^{II}Cl_2$(4-aza[6]helicene)PPh_3] complexes. This unexpected reactivity is explained through a dynamic process (crystallization-induced diastereoselective transformation) and enables a new aspect of reactivity in chiral transition-metal complexes to be addressed.*

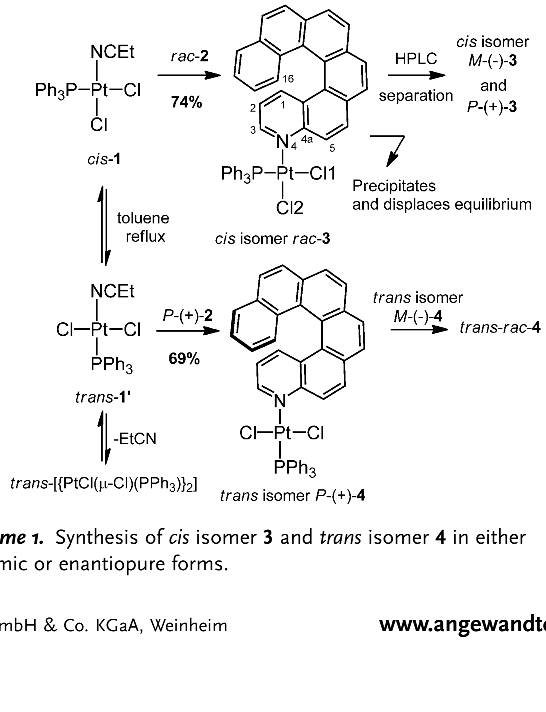
Square-planar (SP-4) platinum(II) complexes of general formula [LL′PtX_2] display the usual *cis–trans* isomerism that is well-known in coordination chemistry.[1] Such isomerism can have important practical implications, such as in the famous case of [$Pt(NH_3)_2Cl_2$], the *cis* isomer of which is an efficient antitumor drug, while the *trans* isomer is ineffective.[2a,b] Therefore the control of the stereochemistry of SP-4 platinum complexes appears to be a pivotal step for the development of efficient drugs as well as innovative molecular materials.[2c,d]

Pure enantiomers and their racemic mixture are known to display different physical properties such as melting points and solubilities.[3] One can take benefit from these different physical properties to optimize, for instance, resolution processes of chiral molecules[3] or to perform uncommon reactivity such as amplification processes.[4a–d] In the liquid phase, identical physical and chemical properties are generally observed for pure enantiomers and their racemic mixture, except in those cases where strong homochiral and heterochiral associations take place.[4e] Furthermore, racemates and pure enantiomers may have different reactivity in solution, such as for example in the asymmetric catalysis, where nonlinear effects may occur.[5]

Herein, we show that the stereochemistry of the complexation of 4-aza[6]helicene ligand (**2**) with [$PtCl_2$(NCEt)PPh_3] **1** depends dramatically on the state of **2**: indeed, racemic **2** leads to *cis*-[$PtCl_2$(**2**)PPh_3] (*cis*-**3**), whilst enantiopure **2** leads to *trans*-[$PtCl_2$(**2**)PPh_3] (*trans*-**4**). In other words, the *cis–trans* isomerism is controlled by the enantiopure or racemic form of the azahelicene ligand. This is, to the best of our knowledge, a brand new aspect of chirality in transition-metal complexes.

Helicene derivatives have recently shown potential as molecular materials owing to their inherent chirality, large-magnitude chiroptical properties, and π-conjugated electronic structure.[6] Following our work aimed at understanding the impact on the chiroptical properties of a metallic ion upon coordination to a helicene ligand,[7a,b,f] we studied the complexation of 4-aza[6]helicene **2**[7c] as a monodentate N-ligand[7d,e] to a platinum(II) center.

For this purpose, *cis*-[$PtCl_2$(NCEt)PPh_3] complex (*cis*-**1**), a square-planar platinum complex bearing a triphenylphosphine ligand and a propionitrile in mutual *cis* position, was used.[8] In refluxing toluene, it isomerizes to the *trans*-[$PtCl_2$(NCEt)PPh_3] (*trans*-**1′**, Scheme 1), which in turn may give the dimeric form *trans*-[{PtCl(μ-Cl)(PPh_3)}$_2$] after releasing EtCN. It is known that by reacting **1** with a pyridine ligand, the *trans*-[$PtCl_2$(py)PPh_3] complex is formed and it does not isomerize to the *cis* form, which is probably due to the *trans* effect of the PPh_3 ligand.[8b] By replacing pyridine with azahelicene as the N donating ligand, an additional stereogenic element is introduced (*P*/*M* helical chirality) to the *cis–trans* isomerism and diastereoisomers *P-cis* and *P-trans* (and their corresponding mirror images *M-cis* and *M-trans*) are expected. 4-Aza[6]helicene **2** was prepared in racemic form according to the well-known photocylization process (see the Supporting Information).[7c] The reaction of [$PtCl_2$-(NCEt)PPh_3] **1** with a slight excess (1.2 equiv) of (±)-**2** in refluxing toluene for one night resulted in the precipitation of a yellow solid with 74% yield. This precipitate was identified as *cis*-isomeric complex **3** (Scheme 1) by multinuclear NMR spectroscopy, ESI-MS, and X-ray crystallography. For instance, in the ^{1}H NMR spectrum, a strongly deshielded doublet appears at 9.56 ppm ($^3J_{H-H} = 9.4$ Hz) corresponding to H5 proton and a doublet of doublet at 8.45 ppm ($^3J_{H-H} = 5.4$,



Scheme 1. Synthesis of *cis* isomer **3** and *trans* isomer **4** in either racemic or enantiopure forms.

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$^{4}J_{H\text{-}H} = 1.4$ Hz) corresponding to H3 (see numbering in Scheme 1). Furthermore, the ^{31}P NMR displays one signal at 6.2 ppm with a ^{195}Pt–^{31}P coupling constant of 3860 Hz. Single crystals were grown by slow evaporation of diisopropyl ether in a CH_2Cl_2 solution of **3.** The latter crystallized in the triclinic $P\bar{1}$ centrosymmetric space group with the presence of *M* and *P* azahelicenes. Its X-ray crystallographic structure depicted in Figure 1 a reveals the square planar geometry around the platinum atom, which is coordinated to two chlorine ligands in a *cis* mutual position, one 4-aza[6]helicene ligand, and one PPh_3. A slight distortion from ideal angles of 90° is observed (N4PtP and N4PtCl1 angles of 94.8° and 85.2° respectively), which is presumably due to steric hindrance of ligands. Furthermore, *trans* influence causes a greater bond length between platinum and the chlorine atom *trans* to phosphine (Pt−Cl1: 2.357 Å) than the corresponding bond with the chlorine *trans* to the nitrogen atom (Pt−Cl2: 2.291 Å). These values are in agreement with similar complexes.[8d,e] Interestingly, weak intramolecular π–π interactions take place between one phenyl of the PPh_3 ligand and the pyridyl ring (centroid–centroid distance 3.852 Å). This interaction is only possible in the *cis* geometry complex and fixes the geometry around the platinum. Furthermore, owing to the steric hindrance of the helix, the PPh_3 is stacked on one side of the pyridyl ring and therefore planar chirality appears with the pyPtCl2 defining the chiral plane.[9] Indeed, torsion angles of −86.16 and −80.93° (p*M* chirality, Figure 1 b) are measured respectively for C3NPtP and C4aNPtCl1 in the *cis*-**3** molecule having the *M*-4-aza[6]helicene ligand, which means that the *M*-helicity induces a fixed p*M*-chiral planar sense.[10] All four possible stereoisomers (two diastereomeric pairs of enantiomers) are depicted in Figure 1 c. This efficient chiral induction from the helix to the planar chirality around the Pt center is also reflected in the chiroptical properties (see below). Finally, looking more into details the crystal packing of **3** reveals a set of several different intermolecular CH···Cl hydrogen bonds that contribute to the cohesion and the stability of the crystal (Figure 1 d). In solution, NOESY experiments performed in CD_2Cl_2 allow the confirmation of contacts between 1) H1 and H16 atoms belonging to opposite sides of the aza[6]helicene moiety and 2) between Ha protons of the PPh_3 ligand and protons H3 and H5 of the aza[6]helicene (Figure 2 a). This indicates that the preferred conformation of racemic *cis*-**3** in the solid state is also stable in solution. Overall, these interactions are responsible for the fixed *cis* geometry, stability, and low solubility in toluene of the racemic complex **3**. Finally, ESI mass spectrometry afforded a peak at *m*/*z* 880.0 corresponding to sodium cationized $[PtCl_2(\mathbf{2})P(Ph)Na]^+$ of elemental composition corresponding to $[C_{43}H_{30}NPCl_2PtNa]^+$ and with an excellent match between the calculated and the experimental isotopic cluster (see the Supporting Information). Tandem MS experiments were carried out on the monoisotopic ion at *m*/*z* 880.0 isolated in the ion trap and allowed to decompose via collision with He gas. Under these conditions, the peak at *m*/*z* 330 was detected, corresponding to protonated **2**, thus confirming the presence of the aza[6]helicene ligand in the complex.

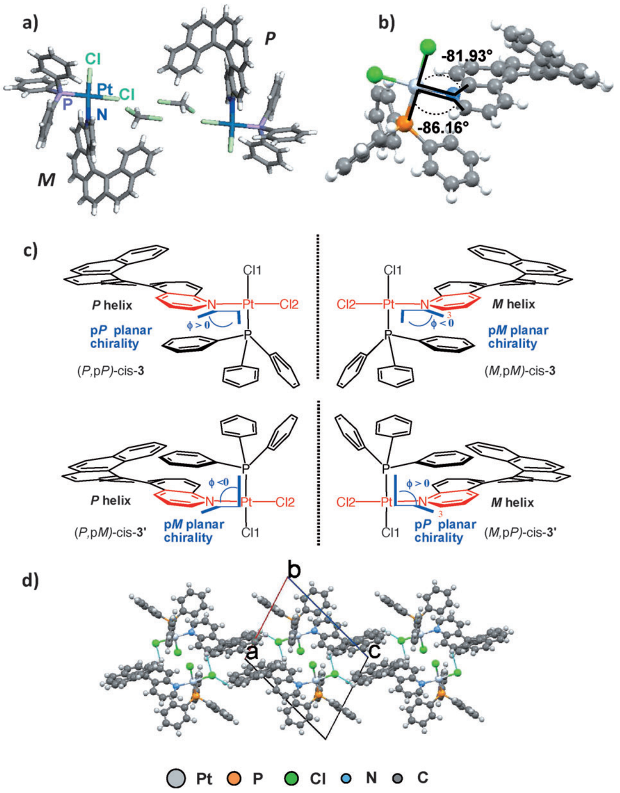

Figure 1. a) X-ray crystallographic structure of racemic *cis*-$[PtCl_2(\mathbf{2})(PPh_3)]$ **3** with the *P* and *M* helicene complexes in the unit cell. b) p*M* planar chirality around the Pt center.[10] c) Drawings emphasizing the helical and planar chiralities and all four possible stereoisomers. The (*P*,p*M*)- and (*M*,p*P*)-*cis*-**3′** stereoisomers are not observed. d) Selected view of the crystal packing and CH···Cl hydrogen bonds.

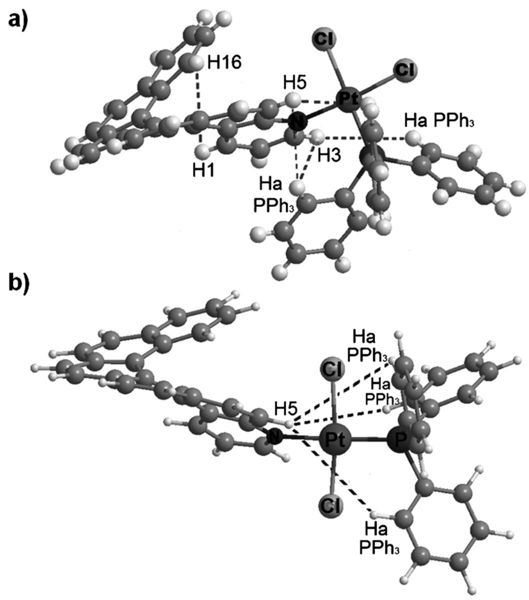

Figure 2. Selected, long-range NOEs (dashed lines) detected in a) *cis*-$[PtCl_2(\mathbf{2})(PPh_3)]$ **3** and b) in *trans*-$[PtCl_2(\mathbf{2})(PPh_3)]$ **4**. The structures of both isomers are based on DFT calculations (the crystal structure coordinates were taken as starting geometry for **3** only).

With the aim to prepare enantiomerically pure complexes, the *M*-(−) and *P*-(+)-**2** enantiomers were separated by HPLC over a chiral stationary phase (see the Supporting Information). Then the reaction between **1** and *P*-(+)-**2** was performed in the same conditions as reported for the racemic ligand (see the Supporting Information). To our surprise, no yellow precipitate was observed and a new compound **4** was isolated in 69% yield after purification, which displayed different ^{1}H, ^{13}C and ^{31}P NMR spectra from *cis*-**3** (see the Supporting Information).

The ^{1}H NMR spectrum displayed one doublet at 9.60 ppm for H5 ($^{3}J_{H\text{-}H}=9.1$ Hz) and one signal (ddd) at 8.90 ppm ($^{3}J_{H\text{-}H}=5.4$, $^{4}J_{H\text{-}H}=1.5$ Hz; $^{4}J_{H\text{-}P}=3.8$ Hz) for H3. ^{31}P NMR displays one signal at 2.6 ppm with a ^{195}Pt–^{31}P coupling constant of 3640 Hz, which is significantly different to that observed for *cis*-**3**. ESI mass spectrometry gave once again a peak at *m/z* 880.0 with isotopic cluster consistent with $[C_{43}H_{30}NPCl_2PtNa]^+$. Isolation and collision-induced fragmentation of monoisotopic *m/z* 880 gave the same fragmentation pattern as before, thus giving arguments in favor of their isomeric relationship and suggesting that the new compound corresponds to the *trans* isomer *P*-(+)-**4** (Scheme 1). Although no crystal structure was obtained for this compound, either enantiopure or racemic, several further information ascertain the *trans* geometry. Long-range NOEs were selectively observed in CD_2Cl_2 solution between Ha-(PPh_3) and H5, but not between Ha(PPh_3) and H3, which is consistent with the *trans* geometry shown in Figure 2b. The assignment of the stereochemistry on the basis of NOEs was supported by DFT calculations on both **3** and **4** (see the Supporting Information). According to the intramolecular NOE theory,[11] the NOE intensity of two H nuclei separated by a distance *r* shows r^{-6} dependency. As a consequence, the threshold of about 5 Å for vanishing NOE is commonly accepted. For the sake of clarity, the average calculated distance of H3 with the Ha protons of the phenyl groups of triphenylphosphine were below and above 5 Å for isomer *cis*-**3** and *trans*-**4**, respectively. Furthermore, coupling constants $^{4}J_{H\text{-}P}$ (3.8 Hz) and $^{5}J_{H\text{-}P}$ (1.4 Hz) are observed in complex **4** for H3 and H2 protons respectively in the ^{1}H NMR spectrum (confirmed by ^{31}P decoupling experiments), which is not observable in the *cis*-**3** isomer. $^{4}J_{H\text{-}P}$ have been reported for complex *trans*-$PtCl_2(SO(CH_3)_2)(PCy_3)$, (Cy = cyclohexyl)[8b] and this further corroborates the hypothesis of a *trans*-geometry for complex *P*-(+)-**4**. Finally, the *trans* nature of **4** was unambigously confirmed thanks to a sample prepared by reacting (±)-**2** with pure *trans*-$[\{Pt(PPh_3)(\mu\text{-}Cl)Cl\}_2]$[8c] which displayed the same ^{1}H and ^{31}P NMR spectra as *P*-(+)-**4**. This compound can only be the racemic *trans* complex owing to the strong *trans* effect of PPh_3 [Eq. (1)]:

$$trans\text{-}[\{Pt(PPh_3)(\mu\text{-}Cl)Cl\}_2] \xrightarrow[CD_2Cl_2]{rac\text{-}\mathbf{2}\ (2\ \text{equiv})} trans\ \text{isomer}\ rac\text{-}\mathbf{4} \quad (1)$$

It is worth mentioning that it was impossible to observe any *P*- or *M*-*cis* isomer **3** from the reaction mixture with enantiomerically pure ligand **2**, even by performing the reaction at −50 °C. Furthermore, heating pure samples of **3** or **4** did not result in any changes, suggesting that **3** and **4** are not in equilibrium. However, deeper inspection of the crude mixture from the reaction of *rac*-**2** with **1** revealed the presence of small quantities (< 5%) of the racemic *trans*-**4** (^{1}H- and ^{31}P NMR spectra in the Supporting Information). As a consequence, the formation of large quantities of *trans*-**4** is prevented by the spontaneous precipitation of *cis*-**3** in refluxing toluene which displaces the **1**/**1′** equilibrium (Scheme 1). This process corresponds to a crystallization induced diastereoselective transformation[12] and originates from the *cis–trans* lability of the starting material.

Finally, the mirror-imaged *trans*-*M*-(−)-**4** complex was obtained starting from *M*-(−)-**2**. On the other hand, the enantiopure *P*-(+) and *M*-(−) *cis* complexes **3** were separated by HPLC over a chiral stationary phase (see the Supporting Information). This illustrates well how the chirality of the ligand (racemic versus enantiopure) can be used to obtain the all sets of *cis*- and *trans*-isomeric Pt complexes in either racemic or enantiopure forms. The chiroptical properties (electronic circular dichroism CD and molar rotation MR) of *P*-(+)/*M*-(−) enantiomers of ligand **2** and *cis* and *trans* isomeric complexes **3** and **4** were then examined (Figure 3).

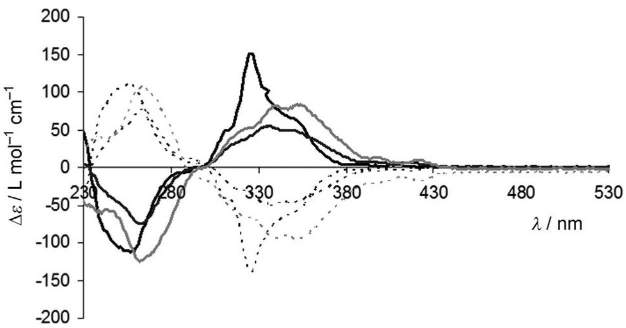

Figure 3. CD spectra of *P*-(+) (plain lines) and *M*-(−) (dotted lines) of ligand **2** (black), *cis* isomer complex **3** (light gray), and *trans* isomer complex **4** (dark gray).

Ligand *P*-**2** displays a strong negative CD-active band at 258 nm ($\Delta\varepsilon = -110\,\text{M}^{-1}\text{cm}^{-1}$) and strong positive bands at 310, 325, and 348 nm (+46, +150, +66 L mol^{-1} cm^{-1}). Complex *P*-**3** displays the same strong negative band of similar intensity (260 nm, $\Delta\varepsilon = -120$ L mol^{-1} cm^{-1}) and strong positive bands at 319, 337, and 351 nm that are red-shifted and of lower intensities (50, 78, 82 L mol^{-1} cm^{-1}) compared to *P*-**2**.

The CD spectrum of complex *P*-**4** shows the same overall shape as *P*-**3** but with lower intensity ($\Delta\varepsilon = -57$ L mol^{-1} cm^{-1} at 258 nm, and 32, 54, 50 L mol^{-1} cm^{-1} at 317, 336, 348 nm, respectively). Two additional weakly CD-active bands at 398 and 420 nm are present in the three compounds. Similarly, lower molar rotation values were measured for *P*-**4** as compared to *P*-**3** (5870 vs. 8215 (±5%), CH_2Cl_2, *C* 0.7–0.4), while ligand *P*-**2** displays values comparable to similar aza[6]helicene derivatives (7735 (±5%), CH_2Cl_2, *C* 1.7).[7b] The bigger chiroptical properties of *cis*-**3** compared to *trans*-**4** may be explained by the fixed planar chirality present in *cis*-**3** that furnishes additional contributions to the ECD and MR values.

In conclusion, the enantiopurity of the starting helicenic ligand (racemic versus enantiopure) triggers its reactivity versus *cis–trans* isomers formation, thus allowing us to prepare the set of all of four *P*-(+)/*M*-(−)-*cis* and *P*-(+)/*M*-(−)-*trans* isomers of complexes [$Pt^{II}Cl_2$(4-aza[6]helicene)PPh_3] and finally to examine their chiroptical properties in relation with their helical/planar chirality. To our knowledge, this is an unprecedented use of chirality in transition-metal complexes, which combines the different solubilities between *cis–trans* stereoisomers with the configurational lability of the starting materials. We think that this can be often encountered in transition-metal complexes and should be more accurately examined when geometrical isomerism (*cis*/*trans*, *fac*/*mer*)[9,10] is combined with chirality (*R*/*S*, Δ/Λ, *M*/*P*).

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